

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 201 607 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication of patent specification: 30.10.91 (51) Int. Cl.<sup>5</sup>: **C07C 65/03, C07C 65/105, C07C 51/15**
- (21) Application number: **85905672.3**
- (22) Date of filing: **09.11.85**
- (86) International application number:  
**PCT/JP85/00626**
- (87) International publication number:  
**WO 86/02924 (22.05.86 86/11)**

The file contains technical information submitted  
after the application was filed and not included in  
this specification

**(54) PROCESS FOR PRODUCING AROMATIC HYDROXYCARBOXYLIC ACID.**

- |  |  |
|--|--|
| <p>(30) Priority: <b>09.11.84 JP 235033/84</b></p> <p>(43) Date of publication of application:<br/><b>20.11.86 Bulletin 86/47</b></p> <p>(45) Publication of the grant of the patent:<br/><b>30.10.91 Bulletin 91/44</b></p> <p>(84) Designated Contracting States:<br/><b>BE CH DE FR GB IT LI NL</b></p> <p>(86) References cited:<br/><b>EP-A- 0 053 824</b><br/><b>JP-A- 4 981 339</b><br/><b>JP-A- 5 535 042</b><br/><b>JP-A-57 197 244</b></p> | <p>(73) Proprietor: <b>Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo</b><br/><b>2-31, Koralbashi</b><br/><b>Higashi-ku Osaka-shi Osaka-fu(JP)</b></p> <p>(72) Inventor: <b>UENO, Ryuzo</b><br/><b>10-27, Nango-cho Nishinomiyashi</b><br/><b>Hyogo 662(JP)</b><br/>Inventor: <b>KANAGAE, Toshiharu</b><br/><b>2138-98, Nishibessho Kuwana-shi</b><br/><b>Mie 551(JP)</b><br/>Inventor: <b>KISHIMOTO, Mitsuyuki</b><br/><b>9-7, Sasagawa Yokkaichi-shi</b><br/><b>Mie 510(JP)</b></p> <p>(74) Representative: <b>Myerscough, Philip Boyd et al</b><br/><b>J.A.Kemp &amp; Co. 14, South Square Gray's Inn</b><br/><b>London, WC1R 5EU(GB)</b></p> |
|--|--|

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**EP 0 201 607 B1**

## Description

The invention relates to a process for selectively producing aromatic hydroxycarboxylic acids, which comprises liquefying an alkali metal salt of an aromatic hydroxy compound with an added aromatic hydroxy compound, followed by reaction with carbon dioxide in a liquid-liquid mixture with a medium.

Aromatic hydroxycarboxylic acids, particularly p-hydroxybenzoic acid, salicylic acid, 2-hydroxy-3-naphthoic acid, etc., have long been known for their usefulness as a raw material for the production of antiseptic and antifungal agents, pharmaceuticals, dyestuffs, pigments and the like, and in recent years, have furthermore acquired increasingly greater importance not only as a starting compound for the synthesis of agricultural chemicals, color developing agents for thermosensitive recording paper, etc. but also as a monomer for aromatic polyesters.

These aromatic hydroxycarboxylic acids have conventionally been produced by means of the so-called Kolbe-Schmitt process involving a vapor-solid phase reaction of an alkali metal salt of an aromatic hydroxy compound with carbon dioxide.

For example, EP-A-66205 describes the preparation of 2-hydroxynaphthalene-3-carboxylic acid by a process which comprises reacting carbon dioxide with a mixture of potassium  $\beta$ -naphtholate,  $\beta$ -naphthol and a reaction medium comprising aliphatic, alicyclic or aromatic hydrocarbons, or aromatic ethers.

JP-A-55-35042 discloses the reaction of carbon dioxide with a mixture comprising sodium  $\beta$ -naphtholate,  $\beta$ -naphthol and an aromatic hydrocarbon and/or an aromatic ether. Those aromatic hydrocarbons include diphenyls and alkyl substituted naphthalenes.

In EP-A-53824, 2-hydroxy-naphthalene 6-carboxylic acid is produced by reaction between carbon dioxide and a mixture comprising potassium  $\beta$ -naphtholate and  $\beta$ -naphthol. The reaction medium may be aliphatic, alicyclic and aromatic hydrocarbons.

Lately, one of the present inventors has improved the said vapor-solid phase reaction process into the liquid-solid phase reaction process making use of a suspension phase, and thus, there has been established a process which permits an industrial-scale, mass-production of such aromatic hydroxycarboxylic acids [refer to the specification of Patent Application No. 39281/1983 (Laid-Open Patent Publication No. 164751/1984)].

The present inventors, with a specific view to further improving the process, carried out repeated research, and found that triaryl based polycyclic aromatic hydrocarbons remaining liquid at ambient

temperature and showing a boiling point of not less than 250°C can produce excellent effects under conditions of an added aromatic hydroxy compound. The finding has led to the completion of this invention.

This invention is directed to a process for producing p-hydroxy benzoic acid..., etc as claim 1.

The present invention aims to provide the following effects:

(1) The media of this invention can suspend thoroughly alkali metal salts of aromatic hydroxy compounds, which permits the complete dehydration of such alkali metal salts of aromatic hydroxy compounds to be performed promptly and at relatively lowered temperatures. Consequently, there can be easily obtained anhydrous alkali metal salts of aromatic hydroxy compounds as a raw material, which, when admixed with aromatic hydroxy compounds and the reaction medium and subjected to a reaction with carbon dioxide, contribute to outstandingly improved yields of the objective compound to be obtained in such a reaction.

(2) A mixture consisting of an anhydrous alkali metal salt of aromatic hydroxy compound, aromatic hydroxy compound and a reaction medium has their components all kept in the liquid form and suspended thoroughly and uniformly under reaction conditions, and can be transported in a quantitative manner, which secures the constant reaction yield in the continuous production process.

(3) The improvement of both yield and selectivity is of utmost importance in the Kolbe-Schmitt reaction, where the production of isomers is always involved and basically inevitable owing to the principle of orientation in the aromatic substitution reaction. In the conventional Kolbe-Schmitt reaction processes, the production of isomers takes place, in spite of the reaction conditions, inclusive of temperature and pressure, being optimally set to minimize the isomer production. However, this invention constitutes a process which keeps the starting material system in the liquid form under reaction conditions and consequently suppresses markedly the production of isomers, permitting the objective compound to be formed in the outstandingly improved selectivity, as compared with the solid-liquid suspension system in the conventional processes.

Thus, in the said reaction where aromatic hydroxycarboxylic acids are formed, the supplementary addition of an aromatic hydroxy compound allows the mutual affinity among three compounds of the aromatic hydroxy compound, the alkali metal salt of an aromatic hydroxy compound and the reaction medium to

be optimally regulated, which can control the orientation direction in the said reaction and can also enhance outstandingly the selectivity.

(4) The reaction media exhibit a high degree of affinity not only for aromatic hydroxy compounds but also for alkali metal salts of aromatic hydroxy compounds, and when mixed with them to form a liquid-liquid mixture of the three components, provide a highly good suspension state, resulting in improvement in the rate of reaction step and the yield of the objective compound.

(5) The process of this invention, which suppresses the conversion into tar of the reaction product in the reaction step and allows the tarry by-products to dissolve in the reaction medium layer, minimizes the contamination of tarry substances into a layer of the alkali metal salt of aromatic hydroxy compound, thus preventing reductions in reaction rate and in yield and proportion of the desired compound owing to contamination of tarry substances.

(6) The above-described reaction media, because of their increased distribution ratio for aromatic hydroxy compounds, allow aromatic hydroxy compounds to immigrate into the water layer to a minimal extent, and consequently facilitate the recovery of aromatic hydroxy compounds. This, coupled with a reduced degree of contamination of tarry substances into the water layer, eliminates the extraction step with organic solvents, etc. for the water layer in the finishing treatment step, while securing the direct production of the objective compound from the water layer.

(7) The above-mentioned reaction media demonstrate excellent thermal stability at increased temperatures even in the presence of alkali metal salts of aromatic hydroxy compounds. Since the loss as a result of thermal degradation is small, it is economically advantageous.

(8) The aforesaid reaction media not only enhances the yield and percentage obtained of the intended product, but also since the media themselves possess superior thermal stability, the production of impurities is reduced, and this facilitates the treatment procedure in the finishing treatment step.

(9) The above-described reaction media, with their higher boiling points, usually bring about no pressure increase owing to vapour pressure of solvent in the reaction step, and offer consequently additional advantage that the reaction vessel can be designed to withstand merely the pressure of carbon dioxide.

The polycyclic aromatic hydrocarbons which are used in this invention are hydrogenated triphenyls or mixtures thereof, and those having a

boiling point of not less than 250°C are desirable.

The alkali metal salts of aromatic hydroxy compounds are potassium phenolate, and sodium 2-naphtholate.

In the Kolbe-Schmitt reaction process, the complete dehydration of a raw material, an alkali metal salt of aromatic hydroxy compound, constitutes one of the most important problems, and inadequate dehydration of the above-described raw material results in a marked decrease in reaction yield. The above raw material can be produced in accordance with the conventional method by the reaction of phenol or 2-naphthol with an alkaline potassium or sodium compound, such as hydroxides, carbonates and hydrogencarbonates of potassium or sodium, and it is particularly advantageous to dehydrate the resulting alkali metal salt of aromatic hydroxy compound in the presence of the above-mentioned reaction medium.

According to this invention, the reaction of an alkali metal salt of aromatic hydroxy compound with carbon dioxide is carried out at a temperature of not lower than 100°C, preferably 120 to 300°C, particularly 150 to 300°C, and at a carbon dioxide pressure of not higher than  $3 \times 10^3$  kPa (30 kg/cm<sup>2</sup> (G)), preferably 98 to 1500 kPa (1 to 15 kg/cm<sup>2</sup> (G)), particularly 200 to 1000 kPa (2 to 10 kg/cm<sup>2</sup> (G)). The addition amount of the aromatic hydroxy compound is normally 0.1 to 2 mole per mole of alkali metal salt of aromatic hydroxy compound. The usage amount of the reaction medium is normally 1 to 5 part by weight against each part by weight of alkali metal salt of aromatic hydroxy compound. The reaction can be conducted either by the batch or continuous process, but it is desirable to carry out the reaction by the continuous process. As the reaction time or the residence time, there can be suitably selected any length of time ranging from several minutes to 15 hours, preferably 10 minutes to 10 hours, particularly 20 minutes to 10 hours.

The finishing treatment can be conducted, for example, by the following procedure. After addition of water to the reaction mixture, the reaction medium layer is separated out, and the dissolved aromatic hydroxy compound can be recovered with a solution of an alkaline potassium or sodium compound as an alkali metal salt of the aromatic hydroxy compound, which is then subjected to reuse. The separated water layer is adjusted in liquid nature with dilute or concentrated sulfuric acid, and the dissolved aromatic hydroxy compound is then extracted with use of toluene or xylene as a reaction medium or organic solvent, as the case may be. The organic solvent layer is washed with a solution of an alkaline potassium or sodium compound to recover it as an alkali metal salt of the aromatic hydroxy compound for reuse as a starting compound. Alternatively, the whole

amount of the organic solvent layer can be distilled off to separate into the organic solvent and the aromatic hydroxy compound, with the latter being reused as a starting compound. These finishing treatment procedures can be suitably selected.

#### Industrial Utilizability

The present invention can offer various advantages as described above under the items (1) through (9), and is of industrial value.

#### Brief Description of the Drawing

Fig. 1 is a schematic flow diagram illustrating the mode of carrying out this invention, wherein the reference numerals 1 and 4 each designates a stirring tank; the numeral 2 a reaction vessel; the numeral 3 a heat exchanger; the numeral 5 a separating tank; the numeral 6 a pH adjustment tank; the numeral 7 an extractor; and the numeral 8 an acid precipitation tank, respectively.

#### Preferred Mode of Carrying out the Present Invention

##### EXAMPLE 1

In a pressure reaction vessel were charged 100g of potassium phenolate, 35g of phenol and 400g of a mixture of hydrogenated triphenyls, and a reaction was allowed to proceed at 250°C and at a carbon dioxide pressure of 690 kPa (7 kg/cm<sup>2</sup>(G)) for 20 minutes, with stirring. The reaction mixture was cooled and charged into 200 ml of water, followed by separation into the reaction medium layer and the water layer at 60°C. The water layer was extracted with 50g of xylene, and the phenol was recovered with an aqueous potassium hydroxide solution from the reaction medium and extraction medium layers. After recovery of phenol, the water layer was made acid with dilute sulfuric acid to give 80.8g of p-hydroxybenzoic acid (having a purity of 100%), with neither salicylic acid nor isophthalic acid being detected as an isomer. The yield based on potassium phenolate was 77.3%, and the recovered phenol was 21.8g, with the selectivity being 99.7%.

##### EXAMPLE 2

In a pressure reaction vessel were charged 166g of sodium 2-naphtholate, 72g of 2-naphthol and 498g of hydrogenated triphenyl, and a reaction was allowed to proceed at 260°C and at a carbon dioxide pressure of 490 kPa (5 kg/cm<sup>2</sup>(G)) for 3 hours, with stirring. The reaction mixture was charged into 800 ml of water, and the resulting

mixture was adjusted to a pH 5.5 with sulfuric acid, followed by separation into the reaction medium layer and the water layer at 85°C. The 2-naphthol was recovered with an aqueous sodium hydroxide solution from the reaction medium layer. After recovery of 2-naphthol, the water layer was adjusted to a pH 2.0 with sulfuric acid at the same temperature, cooled to 40°C and subjected to filtration to give 89.3g of 2-hydroxynaphthalene-3-carboxylic acid. The product was found to contain only 0.1% of 2-hydroxynaphthalene-6-carboxylic acid, with no trace of 2-hydroxynaphthalene-1-carboxylic acid. The yield based on sodium 2-naphtholate was 47.5%, with the selectivity being 99.3%.

##### EXAMPLE 3

A finishing treatment was carried out continuously, while employing the facilities as shown in the drawing. On an hourly basis, 83 kg of sodium 2-naphtholate, 42 kg of 2-naphthol and 166 kg of a mixture of hydrogenated triphenyls were fed to a stirring tank 1, followed by stirring and suspension. The resulting suspension mixture was supplied at a rate of 291 kg/hr to a reaction vessel 2 maintained at a carbon dioxide pressure of 590 kPa (6 kg/cm<sup>2</sup>(G)), and a reaction was allowed to proceed at 260°C, with the residence time being kept at 3 hours. The reaction mixture flowing out of the reaction vessel 2 was cooled with a heat exchanger 3, and mixed with water fed at a rate of 420 l/hr in a stirring tank 4, and the resulting mixture was regulated at a temperature of 85°C and transferred to a separating tank 5, followed by separation into the reaction medium layer and the water layer at 85°C. From the upper reaction medium layer, the 2-naphthol was recovered as sodium naphtholate with use of a recovery apparatus (not shown in the drawing). The lower water layer was adjusted in a pH adjusting tank 6 to a pH 5.5 with dilute sulfuric acid and transferred to an extractor 7, where the 2-naphthol and tar were extracted with 2000 liters of xylene. From the xylene layer, there were recovered the xylene and 2-naphthol by use of a vacuum distillation apparatus (not shown in the drawing). The water layer flowing out of the extractor 7 was transferred to an acid precipitation tank 8, and adjusted to a pH 2.0 with dilute sulfuric acid at 85°C to perform acid precipitation, whereby there was produced 2-hydroxynaphthalene-3-carboxylic acid at a rate of 44.8 kg/hr. The yield based on sodium 2-naphtholate was 47.7%, and 2-naphthol was recovered at a rate of 37.3 kg/hr, with the selectivity being 99.4%.

##### EXAMPLE 4

In a pressure reaction vessel were charged

100g of potassium phenolate, 35g of phenol and 500g of a mixture of hydrogenated triphenyls, and a reaction was allowed to proceed at 250 °C and at a carbon dioxide pressure of 690 kPa (7 kg/cm<sup>2</sup>(G)) for 20 minutes, with stirring. The reaction mixture was cooled and charged into 200 ml of water, followed by separation into the reaction medium layer and the water layer at 60 °C. The water layer was made acid with dilute sulfuric acid to give 81.6g of p-hydroxybenzoic acid (having a purity of 99%). The yield based on potassium phenolate was 77.3%, and the recovered potassium phenolate was 21.0g, with the selectivity being 99.7%.

### Claims

1. A process for producing p-hydroxybenzoic acid or 2-hydroxynaphthalene-3-carboxylic acid, which comprises reacting a liquid mixture composed of
  - (A) potassium phenolate or sodium- $\beta$ -naphtholate
  - (B) a free phenol or a free  $\beta$ -naphthol and
  - (C) a hydrogenated triphenyl in the following proportions:  
 $(B)/(A) = 0.1-2$  (molar ratio) and  
 $(C)/(A) = 1-5$  (weight ratio)
 in the liquid state with carbon dioxide at a pressure of 196 to 980 kPa (2 to 10 kg/cm<sup>2</sup>(G)).
2. A process according to Claim 1 which is carried out continuously.
3. A process according to Claim 1 or 2 wherein, after conclusion of the reaction, the potassium phenolate or sodium  $\beta$ -naphtholate which is dissolved in the separated reaction medium is recovered for reuse.
4. A process according to Claim 1 or 2 wherein, after conclusion of the reaction, the water layer separated after the addition of water is subjected to a pH adjustment, and the dissolved phenol or  $\beta$ -naphthol is extracted with a solvent and recovered for reuse as its alkali metal salt, potassium phenolate or sodium  $\beta$ -naphtholate, after the action of an alkaline potassium or sodium compound.

### Revendications

1. Procédé pour préparer l'acide p-hydroxybenzoïque ou l'acide 2-hydroxynaphtalène-3-carboxylique, qui comprend la réaction d'un mélange liquide, constitué de:
  - (A) phénolate de potassium ou  $\beta$ -naphtolate de sodium,

(B) un phénol libre ou un  $\beta$ -naphtol libre, et  
 (C) un dérivé triphénylique hydrogéné,  
 dans les proportions suivantes:  
 $(B)/(A) = 0,1 \text{ à } 2$  (rapport molaire), et  
 $(C)/(A) = 1 \text{ à } 5$  (rapport en poids)  
 à l'état liquide, avec le dioxyde de carbone, sous une pression de 196 à 980 kPa (2 à 10 kg/cm<sup>2</sup> (pression effective)).

2. Procédé selon la revendication 1, que l'on effectue en continu.
3. Procédé selon la revendication 1 ou 2, dans lequel, après achèvement de la réaction, on récupère, pour le réutiliser, le phénolate de potassium ou le  $\beta$ -naphtolate de sodium qui est dissous dans le milieu réactionnel, après séparation de ce dernier.
4. Procédé selon la revendication 1 ou 2, dans lequel, après achèvement de la réaction, la phase aqueuse séparée après addition d'eau subit un ajustement de pH et le phénol ou le  $\beta$ -naphtol dissous est extrait avec un solvant et récupéré pour réutilisation, sous sa forme de sel de métal alcalin, phénolate de potassium ou  $\beta$ -naphtolate de sodium, après action d'un composé alcalin du potassium ou du sodium.

### Patentansprüche

1. Verfahren zur Herstellung von p-Hydroxybenzoesäure oder 2-Hydroxynaphthalin-3-carbonsäure, umfassend die Umsetzung eines flüssigen Gemisches, bestehend aus
  - (A) Kaliumphenolat oder Natrium- $\beta$ -naphtholat
  - (B) einem freien Phenol oder einem freien  $\beta$ -Naphthol und
  - (C) einem hydrierten Triphenyl in den folgenden Anteilen:  
 $(B)/(A) = 0,1-2$  (Molverhältnis) und  
 $(C)/(A) = 1-5$  (Gewichtsverhältnis)
 in flüssigem Zustand mit Kohlendioxid bei einem Druck von 196 bis 980 kPa (2 bis 10 kg/cm<sup>2</sup> (G)).
2. Verfahren nach Anspruch 1, das kontinuierlich durchgeführt wird.
3. Verfahren nach Anspruch 1 oder 2, wobei nach Abschluß der Reaktion das Kaliumphenolat oder Natrium- $\beta$ -naphtholat, das in dem abgetrennten Reaktionsmedium gelöst ist, für eine erneute Verwendung zurückgewonnen wird.
4. Verfahren nach Anspruch 1 oder 2, wobei nach Abschluß der Reaktion, bei der nach Zugabe

von Wasser abgeschiedenen Wasserschicht  
der pH-Wert eingestellt wird und das gelöste  
Phenol oder  $\beta$ -Naphthol mit einem Lösungs-  
mittel extrahiert und für eine neue Verwendung  
als Alkalisalz, Kaliumphenolat oder Natrium- $\beta$ -  
naphtholatphenolat nach Einwirkung von einer  
alkalischen Kalium- oder Natriumverbindung  
zurückgewonnen wird.

5

10

15

20

25

30

35

40

45

50

55

Fig. 1



